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# Relative Abilities of Fluorine and Chlorine to Stabilize Carbenium Ions.

## Crystal Structures of Two Fluoro-Substituted Carbocations and of As<sub>2</sub>F<sub>11</sub><sup>-</sup>

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### Abstract

The first crystal structures of fluoro-substituted carbocations without heteroatom stabilization and of the As<sub>2</sub>F<sub>11</sub><sup>-</sup> anion are reported. The experimental geometries of the carbenium ions in [(CH<sub>3</sub>)<sub>2</sub>CF]<sup>+</sup>AsF<sub>6</sub><sup>-</sup>, [(m-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)(C<sub>6</sub>H<sub>5</sub>)CF]<sup>+</sup>AsF<sub>6</sub><sup>-</sup> and [(m-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)(C<sub>6</sub>H<sub>5</sub>)CF]<sup>+</sup>As<sub>2</sub>F<sub>11</sub><sup>-</sup> and their comparison with that of the [(o-ClC<sub>6</sub>H<sub>4</sub>)(C<sub>6</sub>H<sub>5</sub>)CCl]<sup>+</sup> cation show that, in accord with previous theoretical calculations, chlorine stabilizes carbenium ions more efficiently than fluorine. The apparent discrepancy between these findings and a previously reached conclusion, based on an analysis of <sup>13</sup>C NMR chemical shift difference data, are reconciled by using the direct <sup>13</sup>C chemical shifts for judging the donor strength of a ligand. The <sup>13</sup>C and <sup>19</sup>F NMR spectra of the [(m-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)(C<sub>6</sub>H<sub>5</sub>)CF]<sup>+</sup> cation were recorded and analyzed with the help of RHF/6-31G(d,p) calculations using the GIAO method. In each of the three fluoro-substituted carbocation crystal structures studied, the carbenium centers are further stabilized by forming two fluorine bridges with the anions, resulting in pseudo-trigonal bipyramidal environments around the carbenium centers. The [F<sub>5</sub>As-F-AsF<sub>5</sub>]<sup>-</sup> anion in [(m-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)(C<sub>6</sub>H<sub>5</sub>)CF]<sup>+</sup>As<sub>2</sub>F<sub>11</sub><sup>-</sup> possesses a symmetric fluorine bridge with an As-F-As angle of 156.5(13)° and staggered AsF<sub>4</sub> groups.

## **Introduction**

Although the nature and structures of carbocations have been studied extensively by electronic structure calculations and spectroscopic techniques,<sup>1</sup> such as NMR or matrix isolation, the number of known crystal structures is quite small.<sup>1,2</sup> Of particular interest in carbocation chemistry is the mechanism and extent to which the highly electron-deficient carbenium center can be stabilized by electron back-donation from its ligands and by bridging to its neighbors.<sup>2</sup> Depending on the nature of the ligand, this stabilization can invoke either p( $\pi$ ) back-donation, if the ligand has a free valence electron pair or involves an aromatic carbon atom, or C-H / C-C hyperconjugation, if the ligand is an alkyl group.<sup>1</sup> If a ligand is highly electronegative, such as fluorine, the inductive electron withdrawing  $\sigma$ -effect is very strong and counteracts the p( $\pi$ ) back-donation, as was demonstrated by natural bond orbital (NBO) analyses for  $\text{CF}_3^{+3,4}$  and  $\text{FCO}^+.$ <sup>4</sup> Unfortunately, the theoretically well characterized  $\text{CF}_3^+$  and  $\text{FCO}^+$  cations cannot be stabilized as salts with presently known Lewis acids,<sup>4</sup> and only one crystal structure was known for a fluoro-substituted carbocation, that of  $[\text{F}_2\overset{\text{S}}{\underset{\text{S}}{\text{C}}} \text{CF}]^+,$ <sup>5</sup> which is stabilized by two sulfur heteroatoms. However, no structure was known for a fluorocarbenium ion without heteroatom stabilization.

The second topic of this study is the  $\text{As}_2\text{F}_{11}^-$  anion. Its existence was first suggested in 1969 based on low-temperature IR<sup>6</sup> and NMR<sup>7</sup> observations. Subsequently, it was positively identified by low-temperature  $^{19}\text{F}$  NMR spectroscopy,<sup>8-11</sup> specific conductivity,<sup>9-12</sup> Raman,<sup>12,13</sup> and x-ray powder diffraction data.<sup>14</sup> However, no exact structural data were available for this interesting anion.

## **Experimental Section**

Materials and Apparatus.  $\alpha,\alpha,\alpha$ -Trifluorotoluene (Aldrich), 2,2-difluoropropane (PCR),  $\text{SO}_2$  (Matheson), and  $\text{AsF}_5$  and  $\text{SO}_2\text{ClF}$  (Ozark Mahoning) were used as received. The HF (Matheson) was dried by storage over  $\text{BiF}_3$ .<sup>15</sup> Volatile compounds were handled either on a Pyrex glass vacuum line equipped with grease-free Kontes glass-Teflon valves or on a previously described<sup>16</sup> stainless steel-Teflon FEP vacuum line. The NMR spectra were recorded in  $\text{SO}_2$  solution at -20°C on a Bruker AM-360 spectrometer using 5 mm Teflon tubes (Wilmad Glass Co.) as sample containers. Single crystals were grown at low temperature by slow cooling of saturated HF solutions, and suitable crystals were selected and mounted with perfluoroether oil in a cold dry nitrogen flow. The diffraction data were collected at -100 °C, using a Siemens/Nicolet/Syntex P2<sub>1</sub> diffractometer with MoK $\alpha$  radiation up to a 2 $\theta$  limit of 55 ° and the computing packages SHELX-86<sup>17</sup> and SHELX-93<sup>18</sup> for refining the data.

Preparation of  $[(\text{CH}_3)_2\text{CF}]^+\text{AsF}_6^-$  (I). In a 0.5 " o.d. Teflon FEP ampule, which was closed by a steel valve, equimolar amounts of  $(\text{CH}_3)_2\text{CF}_2$  and  $\text{AsF}_5$  and a large excess of anhydrous HF (3 mL) were combined at -196 °C. The mixture was warmed to -78 °C, followed by HF removal at -50 °C in a dynamic vacuum, resulting in a white solid that was stable at -50 °C and started to decompose at about -20 °C. It was identified by its crystal structure as  $[(\text{CH}_3)_2\text{CF}]^+\text{AsF}_6^-$ .

Preparation of  $[(m\text{-CF}_3\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CF}]^+\text{AsF}_6^-$  (II) and  $\text{As}_2\text{F}_{11}^-$  (III).  $\alpha,\alpha,\alpha$ -Trifluorotoluene, when combined as described above for (I) with either equimolar amounts or an excess of  $\text{AsF}_5$  in HF,  $\text{SO}_2\text{ClF}$  or  $\text{SO}_2$  solution, gave exclusively  $[(m\text{-CF}_3\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CF}]^+\text{As}_2\text{F}_{11}^-$  (vide infra). With a one-fold or larger excess of  $\alpha,\alpha,\alpha$ -trifluorotoluene, the corresponding  $\text{AsF}_6^-$  salt was obtained. The salts are white solids that are marginally stable at room temperature. (II) and (III) were characterized by their crystal structures and <sup>13</sup>C, <sup>19</sup>F, and <sup>1</sup>H NMR spectra.

## Theoretical Calculations

Various *ab initio* calculations were carried out on the free  $[(\text{CH}_3)_2\text{CF}]^+$ ,  $[\text{m}-(\text{CF}_3\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CF}]^+$ , and  $[\text{As}_2\text{F}_{11}]^-$  ions using the Gaussian 98<sup>19</sup> and ACES II<sup>20</sup> program systems on IBM RS/6000 work stations. The highest level of theory employed for each system was the restricted Hartree-Fock (RHF) method<sup>21</sup> for  $[\text{m}-(\text{CF}_3\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CF}]^+$ , the B3LYP<sup>22</sup> density-functional approach for  $[\text{As}_2\text{F}_{11}]^-$ , and the single- and double-excitation coupled-cluster method<sup>23</sup> with a noniterative treatment of connected triple excitations,<sup>24</sup> denoted CCSD(T), for  $[(\text{CH}_3)_2\text{CF}]^+$ . Several atomic basis sets were employed, including the 6-31G(d,p)<sup>25</sup> set for  $[\text{m}-(\text{CF}_3\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CF}]^+$ , the 6-311+G(d)<sup>26,27</sup> set for  $[\text{As}_2\text{F}_{11}]^-$ , and the 6-311++G(2d,2p)<sup>28</sup> and TZ2P<sup>29</sup> (triple-zeta, double-polarization) sets for  $[(\text{CH}_3)_2\text{CF}]^+$ . Optimized geometries and vibrational spectra were obtained in every case, and for  $[(\text{CH}_3)_2\text{CF}]^+$ , a study was made of the effects of rotating the methyl groups with respect to each other. Additionally, isotropic NMR shieldings for  $[\text{m}-(\text{CF}_3\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CF}]^+$  were calculated at the RHF/6-31G(d,p) level using the gauge-including atomic orbital (GIAO) solution to the gauge-invariance problem.<sup>30</sup> Chemical shifts were obtained by referring these shieldings to those of the standard reference compounds tetramethylsilane and fluorotrichloromethane, which were computed at the same level of theory.

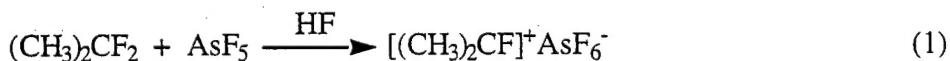
## Results and Discussion

Reliable bond length determinations are uniquely suited for evaluating the relative stabilization of carbenium ions by different ligands. The highly electron-deficient carbenium centers formally possess only six valence electrons and must be stabilized by the formation of partial multiple bonds. Therefore, the observed bond shortenings in carbenium ions, compared to normal single bonds, reveal the relative contributions from different ligands to the stabilization

of a carbenium ion. Whereas methods, such as  $^{13}\text{C}$  NMR shielding measurements, permit evaluation of only the total contribution from all ligands, structure determinations by single crystal x-ray diffraction give the individual contributions from each ligand.

$[(\text{CH}_3)_2\text{CF}]^+\text{AsF}_6^-$  (I). The dimethylfluorocarbenium cation was first observed in 1967 by Olah, Chambers and Comisarow by low-temperature  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectroscopy of solutions of either 2,2-difluoropropane in  $\text{SbF}_5/\text{SO}_2$  or 2-fluoropropene in  $\text{FSO}_3\text{H}/\text{SbF}_5$ .<sup>31,32</sup> Its  $^{13}\text{C}$  NMR spectrum was reported in 1972.<sup>33</sup> Based on the observed  $^{13}\text{C}$  shift differences between the cations,  $(\text{CH}_3)_2\text{CX}^+$  and  $\text{CX}_3^+$ , and the related halocarbons,  $\text{CH}_3\text{CHXCH}_3$  and  $\text{CH}_3\text{CX}=\text{CH}_2$ , it was concluded<sup>33,34</sup> that fluorine is a better back-donor than chlorine. This view was recently challenged, however, in two theoretical studies, one by Frenking and coworkers<sup>3</sup> and another by some of us.<sup>4</sup>

Single crystals of (I) were obtained by slowly cooling equimolar amounts of  $(\text{CH}_3)_2\text{CF}_2$  and  $\text{AsF}_5$  in anhydrous HF solution (1).



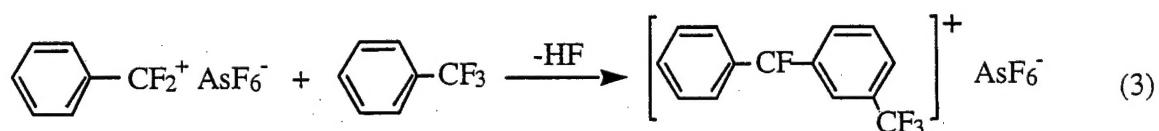
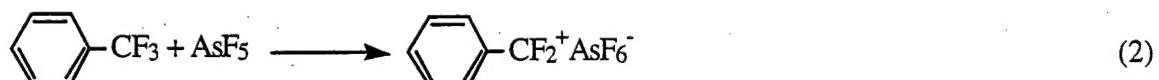
The crystal and structure refinement data, atomic coordinates and equivalent isotropic displacement parameters, and selected bond lengths and angles of (I) are given in Tables 1-3. Full details of the structural results are available as Supplementary Material. The structure of an individual  $[(\text{CH}_3)_2\text{CF}]^+$  cation, connected by two fluorine bridges to neighboring  $\text{AsF}_6^-$  anions, and a packing diagram of (I) are shown in Figures 1 and 2, respectively.

The structure of (I) is ionic, containing discrete  $[(\text{CH}_3)_2\text{CF}]^+$  cations and  $\text{AsF}_6^-$  anions. The  $\text{C}_2\text{CF}$  skeleton of the cation is planar, and its central C(1) atom completes its coordination with two longer, approximately perpendicular fluorine contacts of 2.66 and 2.78 Å, which are significantly shorter than the sum of the C-F van der Waals radii (3.17 Å)<sup>2,35</sup> and involve the F(6)

and (F2') atoms of two different  $\text{AsF}_6^-$  anions (see Figure 1). These fluorine bridges help to populate the empty  $p_z$  orbital of the carbenium center, thereby enhancing its stabilization. They also cause a slight distortion of the  $\text{AsF}_6^-$  anions from octahedral symmetry. The C-F bond length in  $[(\text{CH}_3)_2\text{CF}]^+$  is 1.285(11) Å and is significantly shorter than the average length of 1.333 ± 0.005 Å found for olefinic C-F bonds,<sup>36</sup> indicating substantial electron back-donation from fluorine to the carbenium center. The C(1)-C(2) and C(1)-C(3) bonds of  $[(\text{CH}_3)_2\text{CF}]^+$  were found to be 1.450(13) and 1.413(13) Å, respectively; the apparent difference in their lengths is less than  $3\sigma$  and is believed to be insignificant. This conclusion is supported by an ab initio calculation in which we froze the positions of the two methyl groups such that one C-H bond of one  $\text{CH}_3$  group was coplanar with the unoccupied  $p_z$  orbital on the carbenium carbon and the other  $\text{CH}_3$  group was rotated by 90 °. Even at the highly correlated CCSD(T)/TZ2P level, the maximum differences in the calculated C-C bond lengths were only about 0.001 Å, suggesting that one-sided methyl hyperconjugation,<sup>37</sup> which is strongly angle dependent,<sup>1,38</sup> is very unlikely to cause a difference as large as 0.037 Å in the C-C bond lengths. A similar theoretical analysis was carried out by Schleyer and coworkers for the 2-propyl cation,  $[(\text{CH}_3)_2\text{CH}]^+$ , which showed that at the MP2/6-31G\* level the C-C bond lengths change only by about 0.01 Å for its different rotational isomers.<sup>38</sup> It should be noted that the observed average C-C bond length in  $[(\text{CH}_3)_2\text{CF}]^+$  of 1.432 Å is significantly shorter than the average length of 1.510(5) Å found for the C-C bond in C-C=C type molecules,<sup>36</sup> indicating significant C-C bond shortening due to methyl hyperconjugation.<sup>37</sup>

$[(m\text{-CF}_3\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CF}]^+\text{AsF}_6^-$  (II) and  $[(m\text{-CF}_3\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CF}]^+\text{As}_2\text{F}_{11}^-$  (III). Our original intent was to prepare  $\text{C}_6\text{H}_5\text{CF}_2^+$  from  $\text{C}_6\text{H}_5\text{CF}_3$  by fluoride abstraction with  $\text{AsF}_5$  in HF solution, because the formation of the  $\text{C}_6\text{H}_5\text{CF}_2^+$  cation from  $\text{C}_6\text{H}_5\text{CF}_2\text{Cl}$  in  $\text{SO}_2/\text{SbF}_5$  solutions at –

75 °C had previously been established by  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectroscopy.<sup>39</sup> Surprisingly, it was found that under our conditions, i.e.,  $\text{C}_6\text{H}_5\text{CF}_3$  and  $\text{AsF}_5$  in  $\text{HF}$ ,  $\text{SO}_2$  or  $\text{SO}_2\text{ClF}$  solutions at -20 °C, the only observed products were either (II) or (III), obtained when using an excess of trifluorotoluene or  $\text{AsF}_5$ , respectively. The formation of dimeric cations in (II) and (III) can be explained by a coupling reaction of an intermediate  $\text{C}_6\text{H}_5\text{CF}_2^+$  cation (2) with a second  $\text{C}_6\text{H}_5\text{CF}_3$  molecule (3), a typical Friedel-Crafts benzylation.



This pronounced tendency of  $\text{C}_6\text{H}_5\text{CF}_2^+$  to dimerize resembles that of  $\text{C}_6\text{H}_5\text{CH}_2^+$  to polymerize.<sup>39</sup> Compounds (II) and (III) are white solids that are marginally stable at room temperature.

The structure of the cation in (II) and (III) was established by  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectroscopy, single crystal x-ray diffraction and electronic structure calculations. The  $^{13}\text{C}$  NMR assignments, summarized in Figure 3, are based on the observed  $^{13}\text{C}$ - $^{19}\text{F}$  coupling constants and the chemical shifts from an RHF/6-31G(d,p) calculation<sup>21</sup> at the optimized geometry, which closely resembled the observed one. The calculated  $^{19}\text{F}$  shifts appear to be uniformly about 20

ppm more positive than the observed ones at this level of calculation. The observed  $\Delta \text{C}^+-\text{F}$  shift of 18.0 ppm for (II) is in good agreement with that of 11.5 ppm, previously reported for

$[(C_6H_5)_2CF]^+$ .<sup>39</sup> The observed chemical shifts for the three fluorines of the  $CF_3$  group are, as expected, rotationally averaged.

The agreement between the calculated and observed  $^{13}C$  shifts (Figure 3) is generally quite good and even, in the cases of somewhat larger deviations, the overall shift sequences are retained, i.e., the  $^{13}C$  shifts decrease in the expected<sup>41</sup> order:  $CF^+ > para\text{-}C > ortho\text{-}C > meta\text{-}C > ipso\text{-}C > CF_3$ . The line width of the C2/C6 resonance was found to be larger than the others and to be strongly temperature dependent, possibly due to incipient rotational averaging of C2 and C6 in the given temperature range. The chemical shift of 207 ppm for the carbenium center in (II) agrees well with those of 209 and 212 ppm found for  $[(C_6H_5)_2C(OH)]^+$  and  $[(C_6H_5)_3C]^+$ , respectively,<sup>41</sup> indicating comparable shielding and stabilization by the aryl groups through *ortho*- and *para*- quinoidal resonance structures.

Crystal and refinement data of compounds (II) and (III) are given in Table 1, and their atomic coordinates and selected bond lengths and angles are given in Tables 4-7. Full details of the structural results are available as Supplementary Material. The structures of the individual  $[(m\text{-}CF_3C_6H_4)(C_6H_5)CF]^+$  cations, including their bridging to two neighboring  $AsF_6^-$  or  $As_2F_{11}^-$  anions, and packing diagrams are shown in Figures 4-8.

The structures of (II) and (III) are ionic, containing discrete  $[(m\text{-}CF_3C_6H_4)(C_6H_5)CF]^+$  cations and  $AsF_6^-$  and  $As_2F_{11}^-$  anions, respectively. In the cations, the  $C_2CF^+$  skeleton is again perfectly planar, and the  $-C_6H_4CF_3$  phenyl group is almost coplanar with it, but the unsubstituted phenyl groups in (II) and (III) are twisted by  $39.3^\circ$  and  $47.5^\circ$ , respectively, out of their common planes. As in compound (I), the carbenium centers in (II) and (III) form along their  $p_z$  axes two close fluorine bridges of about 2.78 and 3.04 Å, respectively, with fluorine atoms from two different anions. Whereas the two bridging fluorine atoms of  $AsF_6^-$  in (II) are *cis* to each other,

those of  $\text{As}_2\text{F}_{11}^-$  in (III) are *trans* to each other. The C-F bond length in (II) and (III) is about 1.31 Å and is only slightly shorter than the average C-F bond lengths of  $1.333 \pm 0.005$  and 1.33 Å found for olefinic C-F bonds<sup>35</sup> and the  $\text{CF}_3$  group of this cation, respectively, indicating only weak back-donation from fluorine to the carbenium center. By contrast, the average  $\text{C}^+-\text{C}_{\text{ipso}}$  bond length of 1.43 Å between the carbenium center and the carbon atoms of the phenyl groups is significantly shorter than that of 1.502(7) Å found for the  $\text{C}_6\text{H}_4-\text{CF}_3$  bond in (II) and the average of  $1.47 \pm 0.02$  Å found for  $\text{C}_6\text{H}_5-\text{CO}_2\text{H}$  and salicylic acid,<sup>36</sup> but is similar to those of 1.449(2) and 1.425(10) Å, found for the trityl<sup>40</sup> and  $(o\text{-ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CCl}^+$ <sup>42</sup> cations, respectively. This  $\text{C}^+-\text{C}_{\text{ipso}}$  bond shortening demonstrates that the aromatic substituents play the dominant role in stabilizing the carbenium center in (II) and (III). The average C-C bond distances ( $\text{C}_{\text{ipso}}-\text{C}_{\text{ortho}} = 1.407(7)$ ,  $\text{C}_{\text{ortho}}-\text{C}_{\text{meta}} = 1.373(7)$ ,  $\text{C}_{\text{meta}}-\text{C}_{\text{para}} = 1.395(7)$  Å) in the two phenyl rings are also similar to those found for the trityl<sup>40</sup> and  $(o\text{-ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CCl}^+$ <sup>42</sup> cations.

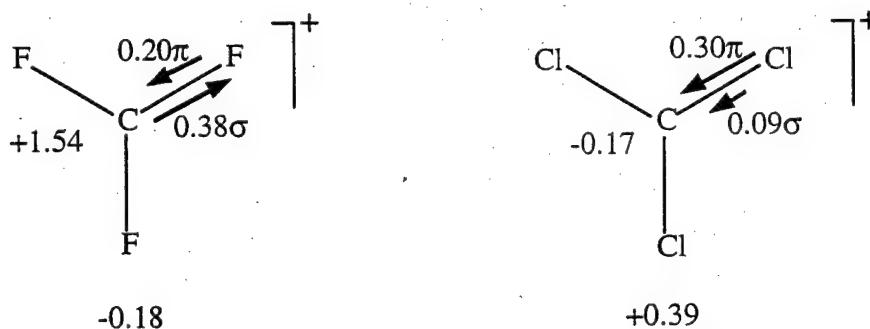
**Relative Ability of Fluorine and Chlorine to Stabilize Carbenium Ions.** A comparison of the bond lengths of (II) and (III) with that of the closely related  $[(o\text{-ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CCl}]^+$  cation<sup>42</sup> and those of the corresponding  $\text{CH}_2\text{CX}=\text{CH}_2$  haloolefins demonstrates that chlorine,  $[\text{R}(\text{C}-\text{Cl}) - \text{R}(\text{C}^+-\text{Cl}) = 0.07$  Å], is a better electron back-donor than fluorine,  $[\text{R}(\text{C}-\text{F}) - \text{R}(\text{C}^+-\text{F}) = 0.02$  Å]. This finding confirms the results of the recent theoretical calculations<sup>3,4</sup> and prompted us to analyze the following assumptions which led to the previous postulate<sup>33,34</sup> of an opposite stabilization effect.

- (i) The stabilizing effect of a halogen ligand is governed by  $p(\pi)$  back-donation from the free valence electron pairs on the halogen and an opposing electron withdrawing inductive  $\sigma$  effect.

(ii) The changes in the  $\sigma$  effect on going from fluorine to the heavier halogens were assumed to be identical for neutral  $\text{CH}_3\text{CHXCH}_3$  and  $\text{CH}_3\text{CX}=\text{CH}_2$  halocarbons and  $>\text{CX}^+$  carbenium ions, i.e., the slopes of the plots of their  $^{13}\text{C}$  NMR shifts against the electronegativity of the halogens were assumed to be identical.

(iii) The deviations from parallelism, observed for the carbenium ions, were attributed exclusively to  $p(\pi)$  back-donation and taken as a measure of the stabilizing power of the corresponding halogen.

The weak point of this postulate is assumption (ii). As was shown by previous theoretical calculations<sup>3,4</sup>,  $\text{C}^+$  is highly electron-deficient and is more electronegative than chlorine. Therefore, in the carbenium cations chlorine becomes both a  $\pi$  and a  $\sigma$  donor, while the more electronegative fluorine is only a  $\pi$  donor and strongly withdraws electron density from the carbon through the  $\sigma$  effect, as previously shown for  $\text{CF}_3^+$  and  $\text{CCl}_3^+$ .



The reversal of direction of the  $\sigma$  effect from fluorine to the heavier halogen atoms occurs only in the carbenium ions but not in the neutral halocarbons in which the halogen ligands are always more electronegative than carbon and carry a negative charge. Consequently, assumption (ii) is deemed invalid.

Since the stabilization of a carbenium center should depend on the *total* electron density supplied by a given ligand to  $\text{C}^+$ , i.e., the sum of the  $\pi$  and the  $\sigma$  effects, and because the  $^{13}\text{C}$

NMR shielding of C<sup>+</sup> is governed by its electron density, the direct <sup>13</sup>C NMR shifts, and not the shift differences between carbenium ions and neutral hydrocarbons, should be used to evaluate the stabilizing effect of ligands on a carbenium center. Inspection of published <sup>13</sup>C NMR shift tables<sup>41</sup> for numerous carbenium ions strongly supports this conclusion.

**The As<sub>2</sub>F<sub>11</sub><sup>-</sup> Anion.** The As<sub>2</sub>F<sub>11</sub><sup>-</sup> anion had previously been identified by spectroscopic<sup>6-13</sup> and conductometric<sup>9,12</sup> studies and x-ray powder diffraction data;<sup>14</sup> the present study is the first crystal structure determination of this anion. The structure of As<sub>2</sub>F<sub>11</sub><sup>-</sup> (Figure 8) resembles in most aspects those found for Sb<sub>2</sub>F<sub>11</sub><sup>-</sup>,<sup>43</sup> with two somewhat distorted AsF<sub>6</sub> octahedra sharing one corner and a symmetric As-F-As bridge forming an angle of 156.5(13) °. The two AsF<sub>6</sub> octahedra in As<sub>2</sub>F<sub>11</sub><sup>-</sup> are staggered with respect to each other, forming dihedral angles of about 46 ° to minimize the F...F repulsions. This staggered arrangement is analogous to that previously found for the isoelectronic [AsF<sub>5</sub>-O-AsF<sub>5</sub>]<sup>2-</sup> anion,<sup>44</sup> which possesses a symmetric As-O-As bridge with an angle of 136 °. The slight tilt of the fluorines of the equatorial AsF<sub>4</sub> planes toward the bridge can be explained by the longer As-F bridge bond being less repulsive than the shorter terminal As-F<sub>ax</sub> bonds. Only one AsF<sub>6</sub> group of As<sub>2</sub>F<sub>11</sub><sup>-</sup> is involved in the formation of two fluorine bridges to two cations causing slight elongations of the As(2)-F(8) and As(2)-F(9) bonds.

After completion of this study, we learned that Minkwitz and Neikes have also obtained a crystal structure of a salt containing an As<sub>2</sub>F<sub>11</sub><sup>-</sup> anion,<sup>45</sup> and that the geometry of their As<sub>2</sub>F<sub>11</sub><sup>-</sup> anion closely resembles that found by us for (III). Although the structures of the As<sub>2</sub>F<sub>11</sub><sup>-</sup> anions in both studies and that of isoelectronic [AsF<sub>5</sub>OAsF<sub>5</sub>]<sup>2-</sup> are very similar, it should be kept in mind that in Sb<sub>2</sub>F<sub>11</sub><sup>-</sup> both the Sb-F-Sb bridge angle and the dihedral angle between the two SbF<sub>6</sub> octahedra are very soft and can vary over a wide range.<sup>43c</sup> A similar behavior cannot be excluded

for  $\text{As}_2\text{F}_{11}^-$ , and additional crystal structures containing this anion will be needed to judge if similarly wide variations are possible for  $\text{As}_2\text{F}_{11}^-$ .

## Conclusions

- (i) The first crystal structures of fluorosubstituted carbocations without heteroatom stabilization and  $\text{As}_2\text{F}_{11}^-$  were determined.
- (ii) It is shown that in the absence of a better donor a fluoroligand can significantly stabilize a carbenium center through back-donation, as evidenced by a shortening of the  $\text{C}^+-\text{F}$  bond in  $(\text{CH}_3)_2\text{CF}^+$  by about 0.05 Å.
- (iii) If aromatic carbon atoms or heteroatoms which are better back-donors are also present, the back-donation from fluorine is strongly diminished, as evidenced by a shortening of the  $\text{C}^+-\text{F}$  bond in (II) by only 0.02 Å.
- (iv) Chlorine is a better back-donor than fluorine, as shown by a comparison of the analogous structures of  $[(m\text{-CF}_3\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CF}]^+$  ( $\Delta \text{C}^+-\text{F} \approx 0.02 \text{ \AA}$  and  $\Delta \text{C}^+-\text{C}_{\text{ipso}} \approx 0.07 \text{ \AA}$ ) and  $[(o\text{-ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CCl}]^+$  ( $\Delta \text{C}^+-\text{Cl} \approx 0.07 \text{ \AA}$  and  $\Delta \text{C}^+-\text{C}_{\text{ipso}} \approx 0.07 \text{ \AA}$ ).
- (v) The crystal structure of  $(\text{CH}_3)_2\text{CF}^+$  also shows strong evidence for stabilization of the carbenium center by methyl-hyperconjugation ( $\Delta \text{C}^+-\text{CH}_3 \approx 0.08 \text{ \AA}$ ).
- (vi) All three fluorosubstituted carbocation structures of this study are further stabilized by fluorine bridging with the counterions. These fluorine bridges are approximately perpendicular to the planar  $\text{C}_2\text{CF}^+$  skeleton and are along the axis of the unoccupied  $p_z$  orbital of  $\text{C}^+$ .
- (vii) The structure of the  $\text{As}_2\text{F}_{11}^-$  anion closely resembles that of isoelectronic  $[\text{AsF}_5\text{OAsF}_5]_2^-$  with a bent symmetric As-F-As bridge and dihedral angles of about 46° (staggered  $\text{AsF}_4^-$  groups).

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**Supporting Information Available:** Tables of structure determination summaries, anisotropic displacement parameters, calculated hydrogen coordinates and isotropic displacement parameters of (I), (II) and (III) in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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**Table 1. Crystal data and structure refinement for  $[(\text{CH}_3)_2\text{CF}]^+[\text{AsF}_6]^-$  (I),  
 $[m-(\text{CF}_3\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CF}]^+[\text{AsF}_6]^-$  (II) and  $[m-(\text{CF}_3\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CF}]^+[\text{As}_2\text{F}_{11}]^-$  (III).**

Compound	I	II	III			
Empirical	$\text{C}_3\text{H}_6\text{AsF}_7$	$\text{C}_{14}\text{H}_9\text{AsF}_{10}$	$\text{C}_{14}\text{H}_9\text{As}_2\text{F}_{15}$			
Formula						
Formula Weight	250.00	442.13	612.05			
Temperature	173(2) K	193(2) K	193(2) K			
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å			
Crystal System	Monoclinic	Triclinic	Monoclinic			
Space Group	$\text{P}2(1)/n$ (#14)	$\text{P}(-1)$ (#2)	$\text{P}2(1)/c$ (#14)			
Unit Cell	$a = 8.854(3)$ Å $\alpha = 90$ deg	$a = 7.8612(14)$ Å $\alpha = 83.157(9)$ deg	$a = 15.101(5)$ Å $\alpha = 90$ deg			
Dimensions	$b = 9.544(3)$ Å $\beta = 108.77(2)$ deg	$b = 8.2778(15)$ Å $\beta = 85.342(10)$ deg	$b = 8.649(2)$ Å $\beta = 99.09(4)$ deg			
	$c = 8.856(3)$ Å $\gamma = 90$ deg	$c = 13.1942(20)$ Å $\gamma = 62.915(10)$ deg	$c = 15.190(7)$ Å $\gamma = 90$ deg			
Volume	$708.6(4)$ Å <sup>3</sup>	$758.6(2)$ Å <sup>3</sup>	$1959.0(12)$ Å <sup>3</sup>			
Z	4	2	4			
Density	2.344 g/cm <sup>3</sup>	1.936 g/cm <sup>3</sup>	2.075 g/cm <sup>3</sup>			
(calculated)						
Absorption	4.866 mm <sup>-1</sup>	2.347 mm <sup>-1</sup>	3.549 mm <sup>-1</sup>			
coefficient						
F(000)	480	432	1176			
Goodness-of-fit on	1.178	1.036	1.019			
$F^2$						
Final R indices	$R_1 = 0.0713$	$wR_2 = 0.1744$	$R_1 = 0.0635$	$wR_2 = 0.1502$	$R_1 = 0.1076$	$wR_2 = 0.2777$
[ $>2\sigma(I)$ ]						
R indices	$R_1 = 0.0800$	$wR_2 = 0.1959$	$R_1 = 0.0831$	$wR_2 = 0.1650$	$R_1 = 0.1617$	$wR_2 = 0.3431$
(all data)						

**Table 2.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[(\text{CH}_3)_2\text{CF}]^+[\text{AsF}_6]^-$ . U(eq) is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	U(eq)
As(1)	1487(1)	2647(1)	3948(1)	17(1)
F(1)	2150(8)	4092(6)	3201(8)	40(2)
F(2)	3363(6)	1906(6)	4427(6)	31(1)
F(3)	1001(7)	1886(6)	2095(7)	34(1)
F(4)	821(7)	1181(6)	4667(7)	35(1)
F(5)	-382(7)	3362(7)	3464(7)	35(1)
F(6)	1996(7)	3396(7)	5798(7)	38(1)
F	-583(6)	2969(6)	-3134(6)	31(1)
C(1)	619(10)	2670(10)	-1905(10)	21(2)
C(2)	1504(12)	3845(10)	-1008(11)	27(2)
C(3)	959(11)	1237(9)	-1556(11)	25(2)

**Table 3. Bond lengths [Å] and angles [deg] for  $[(\text{CH}_3)_2\text{CF}]^+[\text{AsF}_6]^-$ .**

As(1)-F(6)	1.710(5)
As(1)-F(5)	1.712(5)
As(1)-F(1)	1.713(6)
As(1)-F(4)	1.718(5)
As(1)-F(3)	1.718(5)
As(1)-F(2)	1.728(5)
F-C(1)	1.285(11)
C(1)-C(3)	1.413(13)
C(1)-C(2)	1.450(13)
F(1)-As(1)-F(4)	179.0(3)
F(6)-As(1)-F(3)	179.2(3)
F(1)-As(1)-F(3)	89.0(3)
F(4)-As(1)-F(3)	90.0(3)
F(6)-As(1)-F(2)	90.0(3)
F(5)-As(1)-F(2)	179.3(3)
F(1)-As(1)-F(2)	90.1(3)
F(4)-As(1)-F(2)	89.6(3)
F(3)-As(1)-F(2)	89.3(3)
F-C(1)-C(3)	117.3(8)
F-C(1)-C(2)	116.5(8)
C(3)-C(1)-C(2)	126.1(8)
C(1)-F(2')	2.66
C(1)-F(6)	2.78
F(2')...C(1)-F	78.9
F(6)...C(1)-F	76.3
F(2')...C(1)-C(2)	89.5
F(2')...C(1)-C(3)	100.8
F(6)...C(1)-C(2)	85.5
F(6)...C(1)-C(3)	106.8

**Table 4.** Atomic coordinates ( $\times 10^{-4}$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[(m\text{-CF}_3\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CF}]^+[\text{AsF}_6]^-$ . U(eq) is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	U(eq)
As(1)	167(1)	4363(1)	2282(1)	21(1)
F(1)	2448(4)	2645(1)	2530(2)	32(1)
F(2)	-2115(5)	6037(4)	2050(3)	39(1)
F(3)	781(6)	4458(5)	1011(2)	45(1)
F(4)	888(5)	5975(4)	2440(3)	43(1)
F(5)	-440(6)	4255(5)	3560(3)	49(1)
F(6)	-539(5)	2722(5)	2121(3)	46(1)
F(11)	-4735(4)	14004(4)	2239(2)	28(1)
F(12)	-2553(6)	13786(5)	5584(3)	45(1)
F(13)	-1408(6)	11246(5)	6532(3)	47(1)
F(14)	-4427(5)	12868(5)	6434(3)	48(1)
C(1)	-3830(7)	12218(6)	2246(4)	23(1)
C(2)	-2769(8)	12295(7)	5883(4)	28(1)
C(11)	-3466(7)	11537(7)	1273(4)	23(1)
C(12)	-1979(7)	9793(7)	1117(4)	23(1)
C(13)	-1677(8)	9160(7)	176(4)	28(1)
C(14)	-2810(9)	10257(8)	-632(4)	33(1)
C(15)	-4267(8)	12002(8)	-488(4)	31(1)
C(16)	-4591(8)	12647(7)	453(4)	27(1)
C(21)	-3348(7)	11277(6)	3243(4)	24(1)
C(22)	-3275(7)	12211(6)	4045(4)	22(1)
C(23)	-2814(7)	11315(7)	5006(4)	24(1)
C(24)	-2430(8)	9484(7)	5187(4)	26(1)
C(25)	-2546(8)	8562(7)	4401(4)	26(1)
C(26)	-3022(7)	9450(6)	3437(4)	23(1)

**Table 5. Bond lengths [Å] and angles [deg] for [(*m*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)(C<sub>6</sub>H<sub>5</sub>)CF]<sup>+</sup>[AsF<sub>6</sub>].**

As(1)-F(4)	1.789(3)	F(4)-As(1)-F(3)	89.8(2)
As(1)-F(3)	1.710(3)	F(4)-As(1)-F(5)	90.4(2)
As(1)-F(5)	1.717(3)	F(3)-As(1)-F(5)	179.7(2)
As(1)-F(2)	1.720(3)	F(4)-As(1)-F(2)	90.4(2)
As(1)-F(6)	1.725(3)	F(3)-As(1)-F(2)	91.0(2)
As(1)-F(1)	1.734(3)	F(5)-As(1)-F(2)	89.3(2)
F(11)-C(1)	1.316(5)	F(4)-As(1)-F(6)	179.5(2)
F(12)-C(2)	1.331(7)	F(3)-As(1)-F(6)	90.0(2)
F(13)-C(2)	1.326(6)	F(5)-As(1)-F(6)	89.8(2)
F(14)-C(2)	1.349(6)	F(2)-As(1)-F(6)	90.0(2)
C(1)-C(11)	1.420(7)	F(4)-As(1)-F(1)	89.7(2)
C(1)-C(21)	1.431(7)	F(5)-As(1)-F(1)	90.0(2)
C(2)-C(23)	1.502(7)	F(2)-As(1)-F(1)	178.8(2)
C(11)-C(16)	1.406(7)	F(6)-As(1)-F(1)	88.9(2)
C(11)-C(12)	1.410(7)	F(11)-C(1)-C(11)	115.4(4)
C(12)-C(13)	1.366(7)	F(11)-C(1)-C(21)	114.1(4)
C(13)-C(14)	1.393(8)	C(11)-C(1)-C(21)	130.5(4)
C(14)-C(15)	1.399(8)	F(13)-C(2)-F(12)	108.2(5)
C(15)-C(16)	1.369(8)	F(13)-C(2)-F(14)	105.9(5)
C(21)-C(22)	1.402(7)	F(12)-C(2)-F(14)	105.6(4)
C(21)-C(26)	1.408(7)	F(13)-C(2)-C(23)	112.8(4)
C(22)-C(23)	1.376(7)	F(12)-C(2)-C(23)	113.0(5)
C(23)-C(24)	1.398(7)	F(14)-C(2)-C(23)	110.9(5)
C(24)-C(25)	1.390(7)	C(16)-C(11)-C(12)	120.0(5)
C(25)-C(26)	1.379(7)	C(16)-C(11)-C(1)	118.9(5)
		C(12)-C(11)-C(1)	121.1(5)
		C(13)-C(12)-C(11)	119.9(5)
		C(12)-C(13)-C(14)	119.9(5)
		C(13)-C(14)-C(15)	120.6(5)
		C(16)-C(15)-C(14)	120.0(5)
		C(15)-C(16)-C(11)	119.6(5)
		C(22)-C(21)-C(26)	119.6(5)
<b>Bridge bonds:</b>		C(22)-C(21)-C(1)	119.4(5)
C(1) ..F(6)	2.79	C(26)-C(21)-C(1)	120.9(5)
C(1) ..F(1)	2.78	C(23)-C(22)-C(21)	119.7(4)
F(1) ..C(1) ..F(6)	164.8	C(22)-C(23)-C(24)	120.4(5)
F(1) ..C(1) ..F(11)	81.1	C(22)-C(23)-C(2)	120.8(5)
F(6) ..C(1) ..F(11)	84.4	C(24)-C(23)-C(2)	118.8(5)
F(1) ..C(1) ..C(11)	97.1	C(25)-C(24)-C(23)	120.2(5)
F(1) ..C(1) ..C(21)	91.1	C(26)-C(25)-C(24)	119.9(5)
F(6) ..C(1) ..C(11)	93.1	C(25)-C(26)-C(21)	120.1(5)
F(6) ..C(1) ..C(21)	90.8		

Dihedral angle between phenyl groups 39.3

**Table 6.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[(m\text{-CF}_3\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CF}]^+[\text{As}_2\text{F}_{11}]^-$ . U(eq) is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	U(eq)
As(1)	1708(1)	669(2)	2506(1)	47(1)
As(2)	4153(1)	1157(2)	3037(1)	41(1)
F(1)	2914(9)	1304(24)	2652(14)	140(8)
F(2)	644(8)	278(27)	2375(16)	158(9)
F(3)	5254(7)	1165(19)	3326(10)	99(5)
F(4)	1586(16)	2392(18)	2002(14)	156(8)
F(5)	1855(9)	-130(15)	1564(8)	98(3)
F(6)	1969(11)	-982(13)	3047(8)	93(5)
F(7)	1723(12)	1536(17)	3479(11)	111(5)
F(8)	4190(10)	1917(16)	2021(8)	91(4)
F(9)	4104(10)	-619(15)	2560(11)	96(5)
F(10)	3919(12)	398(20)	3942(9)	112(5)
F(11)	4028(9)	2936(14)	3413(10)	86(4)
F(21)	8860(6)	138(13)	1897(6)	50(2)
F(22)	10296(8)	2267(15)	4648(8)	90(3)
F(23)	9432(9)	3643(13)	5265(9)	86(4)
F(24)	9785(10)	1435(18)	5781(9)	95(5)
C(1)	8061(10)	459(17)	2084(10)	36(3)
C(2)	9555(13)	2208(24)	5017(13)	59(5)
C(11)	7356(11)	551(17)	1331(10)	41(4)
C(12)	6607(11)	1390(18)	1365(11)	39(4)
C(13)	5959(11)	1454(21)	621(12)	47(4)
C(14)	6053(13)	713(22)	-131(13)	56(5)
C(15)	6816(12)	-220(21)	-196(10)	46(4)
C(16)	7509(11)	-297(22)	559(9)	45(4)
C(21)	8028(9)	757(16)	2995(9)	30(3)
C(22)	8809(10)	1287(17)	3534(10)	36(3)
C(23)	8787(11)	1571(17)	4427(10)	40(4)
C(24)	8003(11)	1269(20)	4765(10)	43(4)
C(25)	7233(12)	680(19)	4247(12)	44(4)
C(26)	7272(12)	463(19)	3353(11)	44(4)

**Table 7. Bond lengths [Å] and angles [deg] for  $[(m\text{-CF}_3\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CF}]^+[\text{As}_2\text{F}_{11}]$**

Bond distances:

As(1)-F(2)	1.623(13)	C(1)-C(21)	1.42(2)
As(1)-F(5)	1.636(13)	C(1)-C(11)	1.44(2)
As(1)-F(7)	1.655(14)	C(2)-C(23)	1.46(3)
As(1)-F(6)	1.663(11)	C(11)-C(12)	1.35(2)
As(1)-F(4)	1.673(14)	C(11)-C(16)	1.43(2)
As(1)-F(1)	1.881(13)	C(12)-C(13)	1.37(2)
As(2)-F(10)	1.612(13)	C(13)-C(14)	1.34(3)
As(2)-F(3)	1.652(10)	C(14)-C(15)	1.42(3)
As(2)-F(11)	1.663(11)	C(15)-C(16)	1.43(2)
As(2)-F(8)	1.687(12)	C(21)-C(26)	1.36(2)
As(2)-F(9)	1.695(13)	C(21)-C(22)	1.40(2)
As(2)-F(1)	1.874(14)	C(22)-C(23)	1.39(2)
F(21)-C(1)	1.31(2)	C(23)-C(24)	1.39(2)
F(22)-C(2)	1.33(2)	C(24)-C(25)	1.39(2)
F(23)-C(2)	1.32(2)	C(25)-C(26)	1.38(2)
F(24)-C(2)	1.34(2)		

Bond angles:

F(2)-As(1)-F(5)	94.2(10)	F(9)-As(2)-F(1)	87.4(8)
F(2)-As(1)-F(7)	94.5(11)	F(8)-As(2)-F(1)	82.2(9)
F(5)-As(1)-F(7)	171.3(8)	As(2)-F(1)-As(1)	156.5(13)
F(2)-As(1)-F(6)	92.0(9)	F(21)-C(1)-C(21)	115.1(13)
F(5)-As(1)-F(6)	90.9(6)	F(21)-C(1)-C(11)	115.5(13)
F(7)-As(1)-F(6)	88.8(7)	C(21)-C(1)-C(11)	129.3(13)
F(2)-As(1)-F(4)	95.4(11)	F(23)-C(2)-F(24)	105(2)
F(5)-As(1)-F(4)	89.8(9)	F(23)-C(2)-F(22)	104(2)
F(7)-As(1)-F(4)	89.4(10)	F(24)-C(2)-F(22)	105(2)
F(6)-As(1)-F(4)	172.5(10)	F(23)-C(2)-C(23)	113(2)
F(2)-As(1)-F(1)	175.0(10)	F(24)-C(2)-C(23)	115(2)
F(5)-As(1)-F(1)	87.9(8)	F(22)-C(2)-C(23)	113(2)
F(7)-As(1)-F(1)	83.4(9)	C(12)-C(11)-C(16)	123(2)
F(6)-As(1)-F(1)	92.5(9)	C(12)-C(11)-C(1)	121.2(14)
F(4)-As(1)-F(1)	80.1(10)	C(16)-C(11)-C(1)	115(2)
F(10)-As(2)-F(3)	97.0(8)	C(11)-C(12)-C(13)	119(2)
F(10)-As(2)-F(11)	91.8(8)	C(14)-C(13)-C(12)	122(2)
F(3)-As(2)-F(11)	94.0(7)	C(13)-C(14)-C(15)	122(2)
F(10)-As(2)-F(8)	169.2(8)	C(14)-C(15)-C(16)	118(2)
F(3)-As(2)-F(8)	93.7(7)	C(15)-C(16)-C(11)	116(2)
F(11)-As(2)-F(8)	88.6(7)	C(26)-C(21)-C(22)	120.5(14)
F(10)-As(2)-F(9)	89.7(8)	C(26)-C(21)-C(1)	121.1(14)
F(3)-As(2)-F(9)	95.2(8)	C(22)-C(21)-C(1)	118.3(13)
F(11)-As(2)-F(9)	170.4(7)	C(23)-C(22)-C(21)	118.8(14)
F(8)-As(2)-F(9)	88.1(7)	C(24)-C(23)-C(22)	119(2)
F(10)-As(2)-F(1)	87.2(9)	C(24)-C(23)-C(2)	119(2)
F(3)-As(2)-F(1)	175.0(9)	C(22)-C(23)-C(2)	122(2)
F(11)-As(2)-F(1)	83.2(8)	C(23)-C(24)-C(25)	123(2)

C(26)-C(25)-C(24) 116(2)

C(21)-C(26)-C(25) 122(2)

Bridge bonds:

C(1)…F(4)	3.01
C(1)…F(6)	3.07
F(4)…C(1)…F(6)	155.7
F(4)…C(1)…F(12)	79.1
F(6)…C(1)…F(12)	102.0
F(4)…C(1)…C(3)	117.8
F(6)…C(1)…C(3)	84.1
F(4)…C(1)…C(9)	74.6
F(6)…C(1)…C(9)	83.3

Dihedral angles:

between: phenyl groups 47.46(43)  
[As(1)F(1,2,5,7)] and [As(2)F(1,3,9,11)] 44.97(61)  
[As(1)F(1,2,4,6)] and [As(2)F(1,3,9,11)] 49.43(45)  
[As(1)F(1,2,4,6)] and [As(2)F(1,3,8,10)] 40.18(71)  
[As(1)F(1,2,5,7)] and [As(2)F(1,3,8,10)] 51.63(40)  
[As(1)F(4,5,6,7)] and [As(2)F(8,9,10,11)] 14.21(44)

## Diagram Captions

Figure 1. Structure, numbering scheme, and fluorine bridging of the  $[(\text{CH}_3)_2\text{CF}]^+$  cation in (I). The displacement ellipsoids are drawn at the 50% probability level.

Figure 2. Packing diagram for (I).

Figure 3. Observed (calculated)  $^{13}\text{C}$  and  $^{19}\text{F}$  chemical shifts (ppm), multiplicity, and coupling constants (Hz) of the  $[(m\text{-CF}_3\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CF}]^+$  cation.

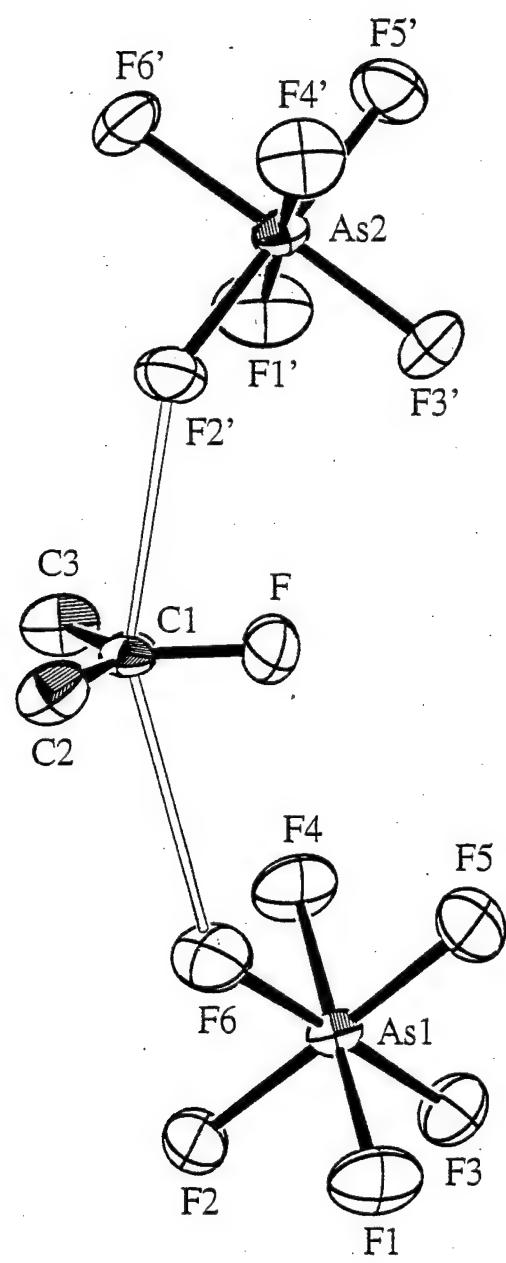
Figure 4. Structure, numbering scheme, and fluorine bridging of the  $[(m\text{CF}_3\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CF}]^+$  cation in (II).

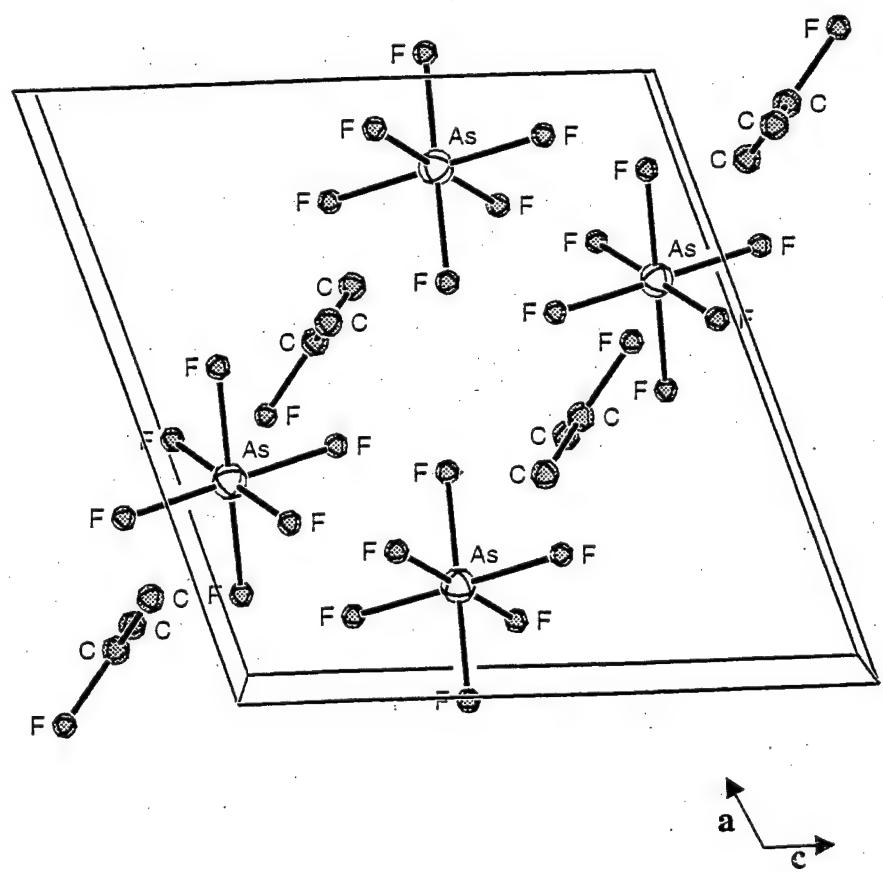
Figure 5. Packing diagram for (II).

Figure 6. Structures and numbering schemes for the ions in (III) with the displacement ellipsoids drawn at the 50% probability level.

Figure 7. Fluorine bridges between C1 of the cation and F4 and F6 of the anions in (III).

Figure 8. Packing diagram for (III).





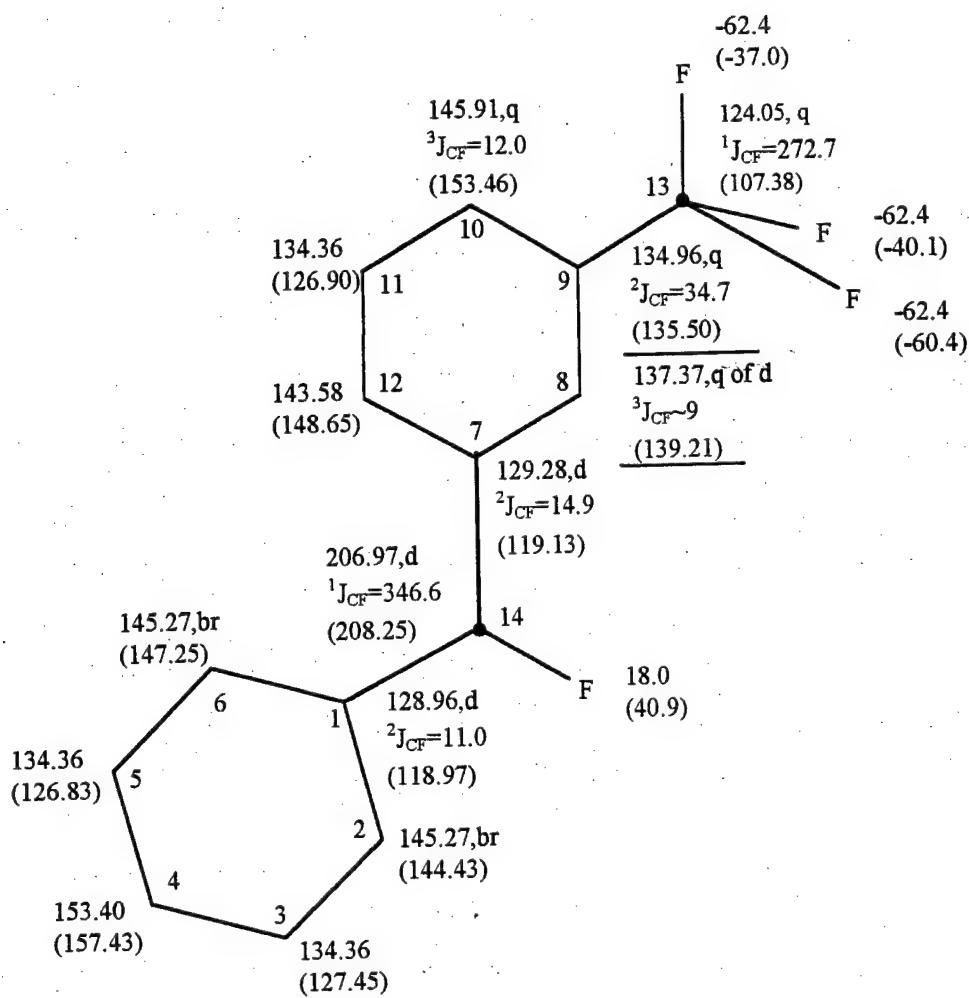
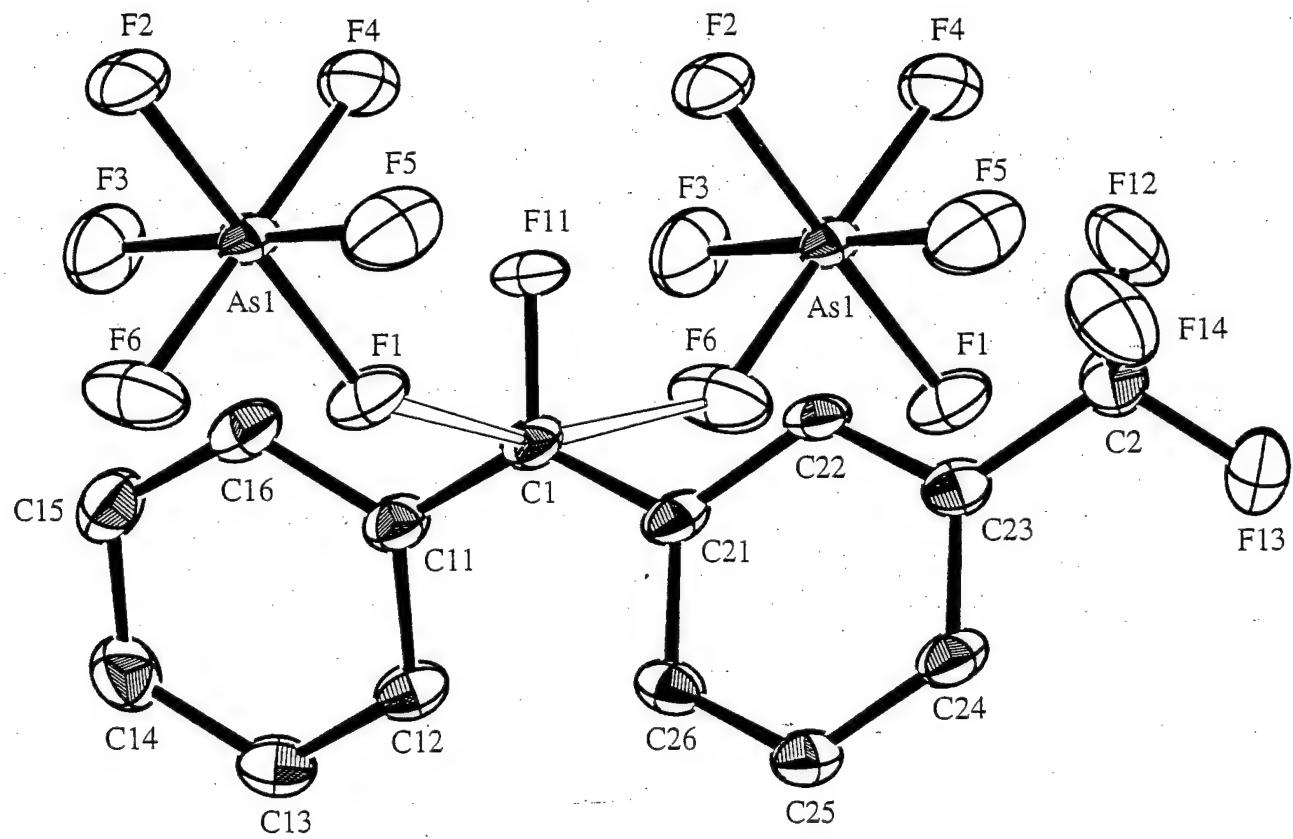
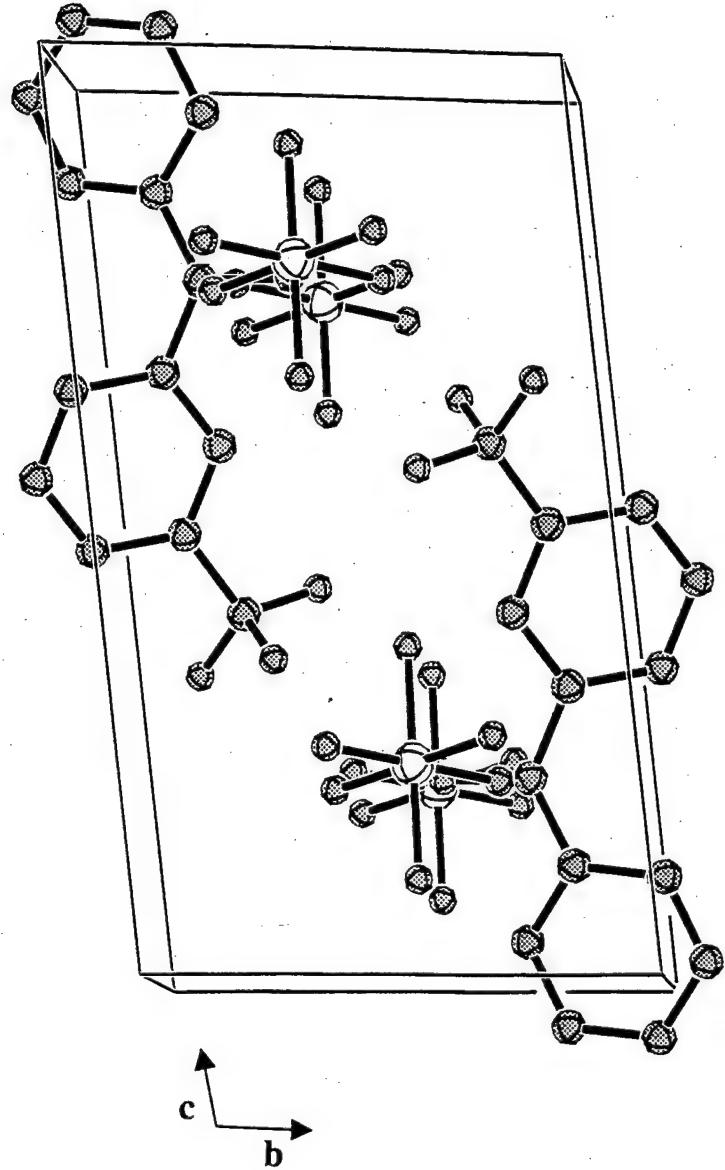


Figure 3





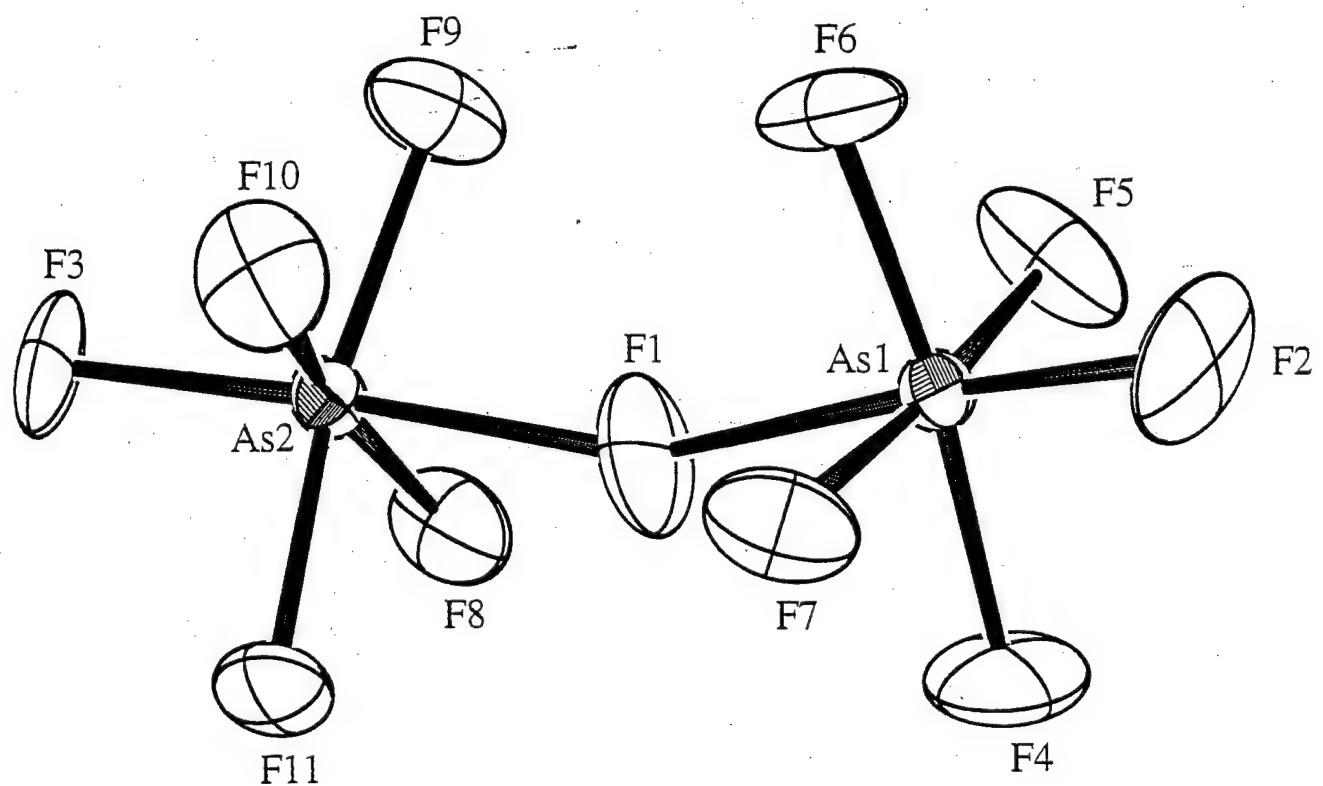
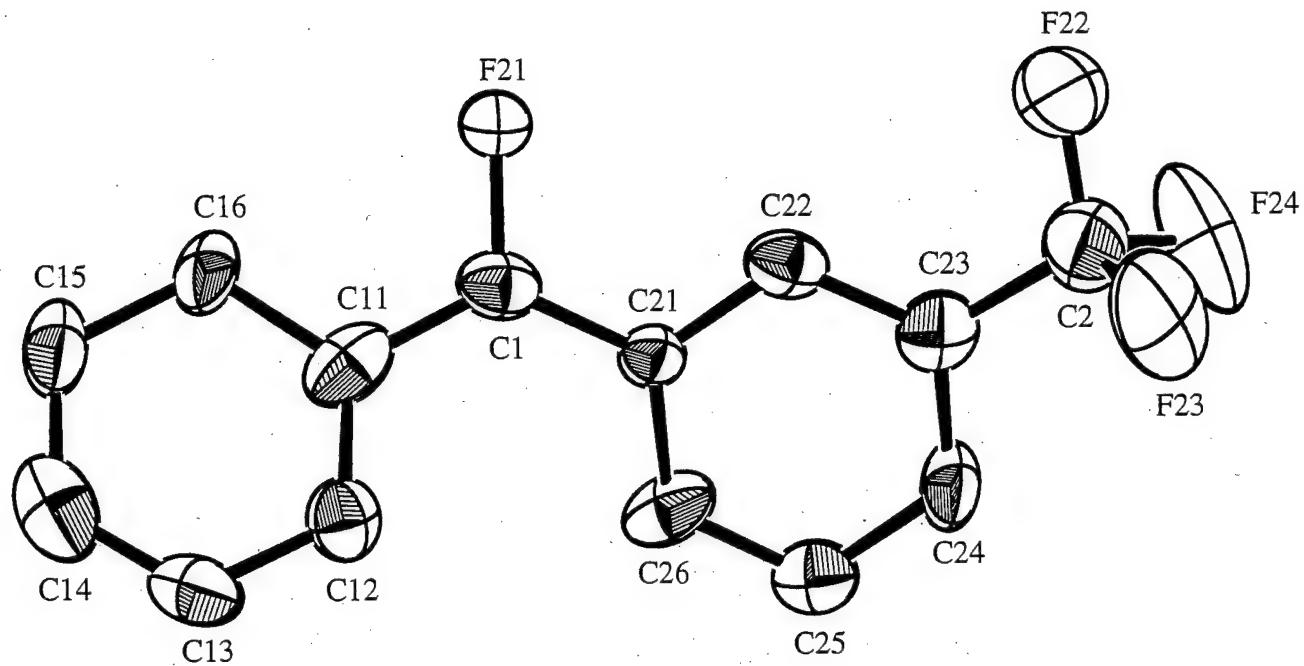


Figure 6

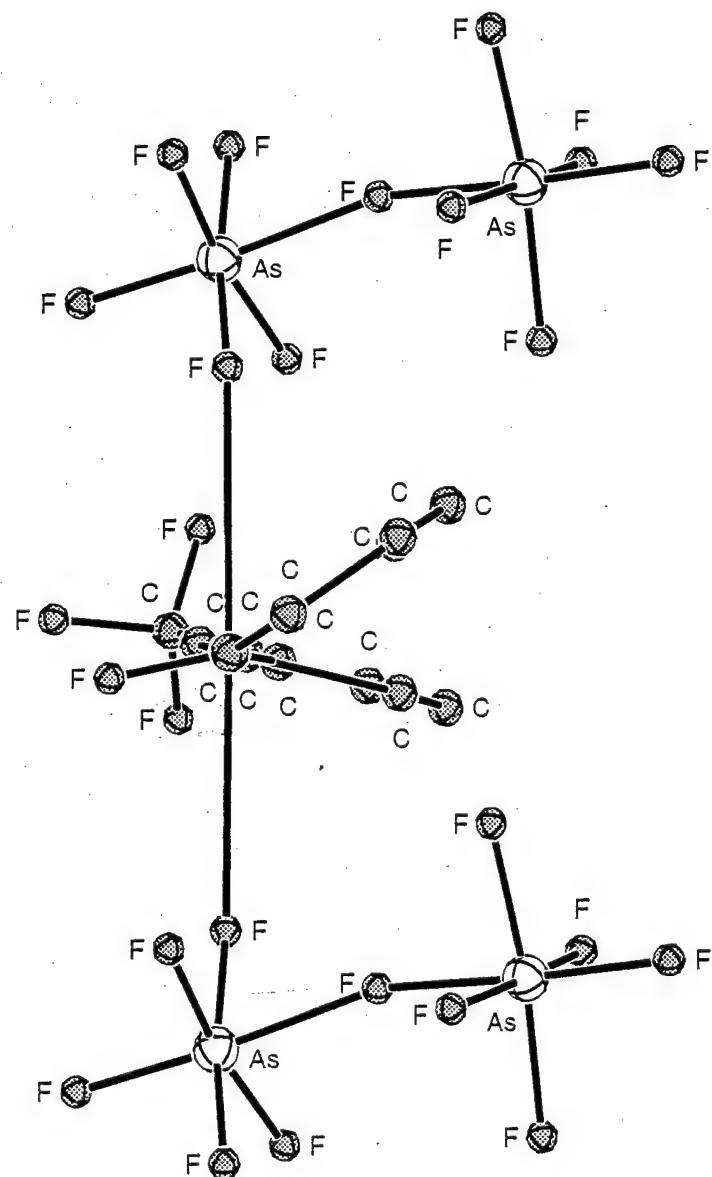


Figure 7

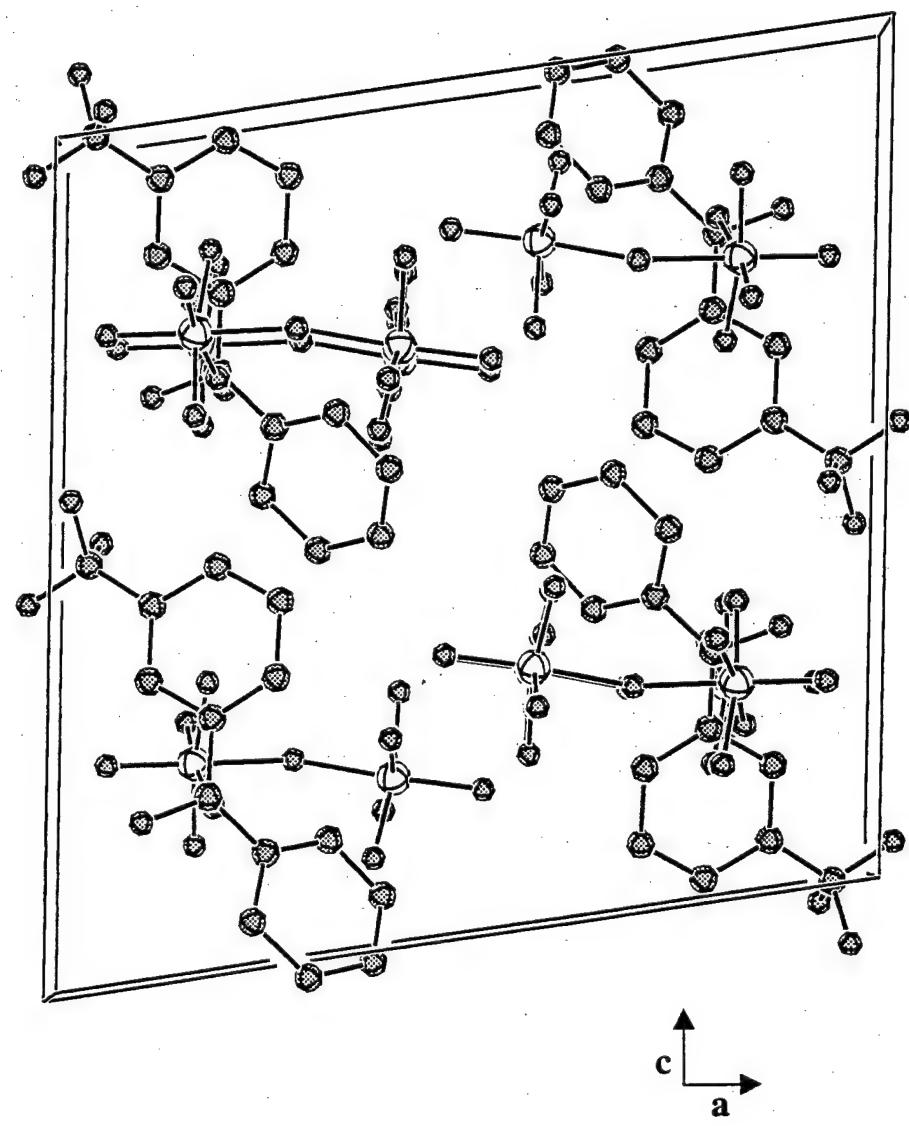


Fig. 8

## SUPPORTING INFORMATION

### Relative Abilities of Fluorine and Chlorine to Stabilize Carbenium Ions.

### Crystal Structures of Two Fluoro-Substituted Carbocations and of As<sub>2</sub>F<sub>11</sub><sup>-</sup>

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#### Abstract

The first crystal structures of fluoro-substituted carbocations without heteroatom stabilization and of the As<sub>2</sub>F<sub>11</sub><sup>-</sup> anion are reported. The experimental geometries of the carbenium ions in [(CH<sub>3</sub>)<sub>2</sub>CF]<sup>+</sup>AsF<sub>6</sub><sup>-</sup>, [(m-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)(C<sub>6</sub>H<sub>5</sub>)CF]<sup>+</sup>AsF<sub>6</sub><sup>-</sup> and [(m-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)(C<sub>6</sub>H<sub>5</sub>)CF]<sup>+</sup>As<sub>2</sub>F<sub>11</sub><sup>-</sup> and their comparison with that of the [(o-ClC<sub>6</sub>H<sub>4</sub>)(C<sub>6</sub>H<sub>5</sub>)CCl]<sup>+</sup> cation show that, in accord with previous theoretical calculations, chlorine stabilizes carbenium ions more efficiently than fluorine. The apparent discrepancy between these findings and a previously reached conclusion, based on an analysis of <sup>13</sup>C NMR chemical shift difference data, are reconciled by using the direct <sup>13</sup>C chemical shifts for judging the donor strength of a ligand. The <sup>13</sup>C and <sup>19</sup>F NMR spectra of the [(m-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)(C<sub>6</sub>H<sub>5</sub>)CF]<sup>+</sup> cation were recorded and analyzed with the help of RHF/6-31G(d,p) calculations using the GIAO method. In each of the three fluoro-substituted carbocation crystal structures studied, the carbenium centers are further stabilized by forming two fluorine bridges with the anions, resulting in pseudo-trigonal bipyramidal environments around the carbenium centers. The [F<sub>5</sub>As-F-AsF<sub>5</sub>]<sup>-</sup> anion in [(m-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)(C<sub>6</sub>H<sub>5</sub>)CF]<sup>+</sup>As<sub>2</sub>F<sub>11</sub> possesses a symmetric fluorine bridge with an As-F-As angle of 156.5(13) ° and staggered AsF<sub>4</sub> groups.

**Table S1. Crystal data and structure refinement for  $[(\text{CH}_3)_2\text{CF}]^+[\text{AsF}_6]^-$**

Empirical formula	$\text{C}_3\text{H}_6\text{AsF}_7$		
Formula Weight	250.00		
Temperature	173(2) K		
Wavelength	0.71073 Å		
Crystal System	Monoclinic		
Space Group	$\text{P}2(1)/n$ (#14)		
Unit Cell Dimensions	$a = 8.854(3)$ Å	$\alpha = 90$ deg.	
	$b = 9.544(3)$ Å	$\beta = 108.77(2)$ deg.	
	$c = 8.856(3)$ Å	$\gamma = 90$ deg.	
Volume	$708.6(4)$ Å <sup>3</sup>		
Z	4		
Density (calculated)	2.344 g/cm <sup>3</sup>		
Absorption coefficient	4.866 mm <sup>-1</sup>		
F(000)	480		
Theta range for data collection	2.83 to 27.54 deg.		
Index ranges	$-5 \leq h \leq 11, -12 \leq k \leq 12,$ $-11 \leq l \leq 11$		
Reflections collected	1994		
Independent Reflections	1502 [R(int) = 0.0614]		
Refinement method	Full-matrix least squares on F <sup>2</sup>		
Data/restraints/parameters	1489 / 0 / 103		
Goodness-of-fit on F <sup>2</sup>	1.178		
Final R indices [I>2 sigma (I)]	R1 = 0.0713, wR2 = 0.1744		
R indices (all data)	R1 = 0.0800, wR2 = 0.1959		
Largest diff. peak and hole	1.766 and -2.255 e·Å <sup>-3</sup>		

**Table S2. Anisotropic displacement parameters ( $\text{A}^2 \times 10^3$ ) for  $\text{[(CH}_3\text{)}_2\text{CF}]^+[\text{AsF}_6]^-$ . The anisotropic displacement factor exponent takes the form:  $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2hk a^* b^* U_{12}]$**

	U11	U22	U33	U23	U13	U12
As(1)	19(1)	16(1)	17(1)	0(1)	9(1)	-1(1)
F(1)	53(4)	24(3)	56(4)	8(3)	33(3)	-4(3)
F(2)	25(3)	42(3)	29(3)	4(3)	12(2)	11(2)
F(3)	39(3)	45(3)	20(2)	-8(2)	11(2)	-2(3)
F(4)	46(3)	20(3)	43(3)	10(2)	22(3)	-5(2)
F(5)	28(3)	40(3)	39(3)	3(3)	13(2)	15(2)
F(6)	37(3)	52(4)	27(3)	-19(3)	16(2)	-10(3)
F	26(3)	44(3)	19(2)	-2(2)	5(2)	3(2)
C(1)	19(4)	29(5)	20(4)	3(3)	12(3)	6(3)
C(2)	36(5)	22(4)	25(4)	-3(4)	12(4)	-10(4)
C(3)	34(5)	13(4)	33(5)	-6(3)	17(4)	-5(3)

**Table S3. Calculated hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{A}^2 \times 10^3$ ) for  $[(\text{CH}_3)_2\text{CF}]^+[\text{AsF}_6]^-$ .**

	x	y	z	U(eq)
H(2A)	2603(20)	3772(41)	-950(74)	41
H(2B)	1430(72)	3837(44)	49(28)	41
H(2C)	1066(55)	4704(10)	-1531(7)	41
H(3A)	1417(72)	1116(13)	-424(13)	38
H(3B)	1699(61)	918(20)	-2070(65)	38
H(3C)	-9(16)	704(12)	-1937(70)	38

**Table S4. Crystal data and structure refinement for  $[(m\text{-CF}_3\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CF}]^+[\text{AsF}_6]^-$ .**

Empirical formula	$\text{C}_{14}\text{H}_9\text{AsF}_{10}$		
Formula Weight	442.13		
Temperature	193(2) K		
Wavelength	0.71073 Å		
Crystal System	Triclinic		
Space Group	$P(-1)$ (#14)		
Unit Cell Dimensions	$a = 7.8612(14)$ Å	$\alpha = 83.157(9)$ deg.	
	$b = 8.2778(15)$ Å	$\beta = 85.342(10)$ deg.	
	$c = 13.1942(20)$ Å	$\gamma = 62.915(10)$ deg.	
Volume	$758.6(2)$ Å <sup>3</sup>		
Z	2		
Density (calculated)	1.936 g/cm <sup>3</sup>		
Absorption coefficient	2.347 mm <sup>-1</sup>		
F(000)	432		
Theta range for data collection	2.78 to 27.50 deg.		
Index ranges	$-10 \leq h \leq 9, -10 \leq k \leq 10,$ $-17 \leq l \leq 17$		
Reflections collected	3960		
Independent Reflections	3208 [R(int) = 0.0406]		
Refinement method	Full-matrix least squares on F <sup>2</sup>		
Data/restraints/parameters	3208 / 0 / 226		
Goodness-of-fit on F <sup>2</sup>	1.036		
Final R indices [I>2 sigma (I)]	R1 = 0.0635, wR2 = 0.1502		
R indices (all data)	R1 = 0.0831, wR2 = 0.1650		
Largest diff. peak and hole	1.574 and -1.923 e.Å <sup>-3</sup>		

**Table S5.** Anisotropic displacement parameters ( $\text{A}^2 \times 10^3$ ) for  $[(m\text{-CF}_3\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CF}]^+[\text{AsF}_6]^-$ .  
The anisotropic displacement factor exponent takes the form:  $-2\pi^2[h^2a^{*2}\text{U}11 + \dots + 2hka^*b^*\text{U}12]$

	U11	U12	U33	U23	U13	U12
As(l)	17(l)	15(1)	27(l)	-2(l)	-3(1)	-2(1)
F(l)	20(2)	23(2)	43(2)	3(l)	-4(1)	-2(1)
F(2)	23(2)	24(2)	62(2)	-4(2)	-12(2)	-2(1)
F(3)	50(2)	47(2)	24(2)	-2(l)	0(2)	-10(2)
F(4)	40(2)	24(2)	65(2)	-4(2)	-20(2)	-12(2)
F(5)	49(2)	41(2)	34(2)	-3(2)	12(2)	-2(2)
F(6)	32(2)	29(2)	83(3)	-16(2)	4(2)	-16(2)
F(11)	30(2)	12(l)	35(2)	-2(1)	-3(1)	-2(1)
F(12)	72(3)	39(2)	37(2)	-8(2)	-4(2)	-35(2)
F(13)	48(2)	43(2)	41(2)	-6(2)	-21(2)	-9(2)
F(14)	38(2)	60(2)	50(2)	-33(2)	16(2)	-21(2)
C(1)	15(2)	16(2)	35(3)	0(2)	-7(2)	-4(2)
C(2)	22(3)	30(3)	29(3)	-7(2)	0(2)	-7(2)
C(11)	19(3)	19(2)	28(3)	-1(2)	-2(2)	-5(2)
C(12)	19(3)	19(2)	27(2)	1(2)	4(2)	-5(2)
C(13)	25(3)	22(2)	33(3)	-7(2)	5(2)	-7(2)
C(14)	44(4)	33(3)	25(3)	-4(2)	-1(2)	-19(3)
C(15)	32(3)	30(3)	30(3)	7(2)	-9(2)	-13(2)
C(16)	20(3)	21(2)	34(3)	3(2)	-4(2)	-5(2)
C(21)	17(2)	17(2)	28(2)	-1(2)	-2(2)	0(2)
C(22)	16(2)	11(2)	32(3)	-1(2)	-2(2)	-2(2)
C(23)	16(3)	20(2)	29(3)	-6(2)	1(2)	-1(2)
C(24)	23(3)	19(2)	26(2)	0(2)	-1(2)	-1(2)
C(25)	25(3)	18(2)	31(3)	-3(2)	1(2)	-5(2)
C(26)	19(3)	18(2)	30(3)	-8(2)	3(2)	-7(2)

**Table S6. Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{Å}^2 \times 10^3$ ) for  $[(m\text{-CF}_3\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CF}]^+[\text{AsF}_6]^-$ .**

	x	y	z	U(eq)
H(12)	-1233	9103	1634	28
H(13)	-838	8140	87	34
H(14)	-2592	9821	-1283	40
H(15)	-5006	12716	-1025	38
H(16)	-5400	13630	535	33
H(22)	-3507	13288	3943	26
H(24)	-2081	8853	5865	31
H(25)	-2330	7482	4512	32
H(26)	-3104	8971	3025	28

**Table S7. Crystal data and structure refinement for  $[(m\text{-CF}_3\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CF}]^+[\text{As}_2\text{F}_{11}]^-$ .**

Empirical formula	$\text{C}_{14}\text{H}_9\text{As}_2\text{F}_{15}$		
Formula Weight	612.05		
Temperature	193(2) K		
Wavelength	0.71073 Å		
Crystal System	Monoclinic		
Space Group	$\text{P}2(1)/c$ (#14)		
Unit Cell Dimensions	$a = 15.101(5)$ Å	$\alpha = 90$ deg.	
	$b = 8.649(2)$ Å	$\beta = 99.09(4)$ deg.	
	$c = 15.190(7)$ Å	$\gamma = 90$ deg.	
Volume	$1959.0(12)$ Å <sup>3</sup>		
Z	4		
Density (calculated)	2.075 g/cm <sup>3</sup>		
Absorption coefficient	3.549 mm <sup>-1</sup>		
F(000)	1176		
Theta range for data collection	2.72 to 27.50 deg.		
Index ranges	$-16 \leq h \leq 16, -8 \leq k \leq 11,$ $-19 \leq l \leq 19$		
Reflections collected	4710		
Independent Reflections	3703 [R(int) = 0.0742]		
Refinement method	Full-matrix least squares on F <sup>2</sup>		
Data/restraints/parameters	3686 / 0 / 290		
Goodness-of-fit on F <sup>2</sup>	1.019		
Final R indices [I>2 sigma (I)]	R1 = 0.1076, wR2 = 0.2777		
R indices (all data)	R1 = 0.1617, wR2 = 0.3431		
Largest diff. peak and hole	1.935 and -0.848 e.Å <sup>-3</sup>		

**Table S8. Anisotropic displacement parameters ( $\text{Å}^2 \times 10^3$ ) for  $[(m\text{-CF}_3\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CF}]^+[\text{As}_2\text{F}_{11}]^-$ .  
The anisotropic displacement factor exponent takes the form:  $-2\pi^2[h^2a^{*2}\text{U}11 + \dots + 2hka^*b^*\text{U}12]$**

	U11	U22	U33	U23	U13	U12
As(1)	35(1)	42(1)	63(1)	5(1)	3(1)	-5(1)
As(2)	31(1)	42(1)	51(1)	-9(1)	10(1)	0(1)
F(1)	48(8)	159(17)	203(20)	-12(15)	-15(10)	-34(9)
F(2)	23(7)	201(21)	247(23)	78(19)	12(9)	-5(9)
F(3)	29(6)	144(13)	114(11)	15 (10)	-19(6)	10(7)
F(4)	232(23)	58(9)	166(18)	49(11)	-2(16)	1(12)
F(5)	141(8)	96(8)	60(8)	-5(7)	27(7)	-42(7)
F(6)	165(14)	48(7)	66(7)	12(6)	21(8)	32(8)
F(7)	147(14)	82(10)	116(12)	-43(9)	58 (1)	3(9)
F(8)	132(12)	86(9)	56(7)	-1(7)	16(7)	-21(9)
F(9)	96 (1)	65(8)	143(13)	-32(8)	62(9)	-18(7)
F(10)	145(14)	131(13)	64(8)	16(8)	32(9)	-24(11)
F(11)	86(9)	58(7)	116 (1)	-30(7)	18(8)	13(6)
F(21)	28(5)	88(7)	36(5)	-12(5)	8(4)	0(5)
F(22)	54(8)	128(8)	85(8)	-49(7)	5(6)	-22(7)
F(23)	94(9)	49(7)	103(10)	-37(7)	-24(8)	8(6)
F(24)	93(9)	98(11)	76(8)	18(8)	-45(7)	-18(8)
CM	30(8)	32(8)	47(9)	-1(7)	9(6)	-3(6)
C(2)	52(10)	68(13)	56(12)	-1(11)	7(9)	14(9)
C(11)	53(10)	33(8)	43(8)	4(7)	25(7)	-11(7)
C(12)	44(9)	36(8)	38(8)	-2(7)	3(7)	-3(7)
C(13)	31(8)	56 (1)	55(11)	13(9)	6(8)	7(8)
C(14)	56(11)	58(11)	48(10)	23(9)	-6(9)	-15(10)
C(15)	57(11)	57 (1)	25(7)	-2(7)	8(7)	-13(9)
C(16)	40(9)	71(2)	26(8)	-8(8)	14(7)	-28(8)
C(21)	29(7)	31(7)	29(7)	0(6)	4(6)	7(6)
C(22)	28(8)	29(7)	52(9)	-8(7)	7(7)	2(6)
C(23)	48(9)	25(7)	44(9)	-2(6)	3(7)	11(7)
C(24)	53(10)	51(10)	22(7)	2(7)	-1(7)	3(8)
C(25)	40(9)	44(9)	50 (1)	1(8)	14(8)	1(7)
C(26)	54(10)	45(9)	37(8)	21(7)	22(8)	17(8)

**Table S9. Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[(m\text{-CF}_3\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CF}]^+[\text{As}_2\text{F}_{11}]^-$ .**

	x	y	z	U(eq)
H(12)	6529(18)	1928(102)	1898(99)	47
H(13)	5579(78)	1875(88)	635(12)	57
H(14)	5647(90)	801(30)	-581(101)	67
H(15)	6856(14)	-702(100)	-656(92)	56
H(16)	8272(152)	-1129(166)	546(10)	53
H(22)	9389(103)	1463(37)	3269(49)	44
H(24)	7991(12)	1483(44)	5408(123)	52
H(25)	6749(100)	459(47)	4477(48)	53
H(26)	6760(102)	100(76)	2979(76)	53